REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
19-05-2016	Final Report	13-Dec-2015 - 12-May-2016

4. TITLE AND SUBTITLE
Final Report: Symposium "Supramolecular Assemblies on Surface: Nanopatterning, Functionality and Reactivity"

5a. CONTRACT NUMBER
W911NF-16-1-0036

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

6. AUTHORS
Dmitrii Perepichka

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
McGill University
845 Sherbrooke Street West, 2nd Floor

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
68367-CH-CF.1

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
Funds are requested to provide support for the "Supramolecular Assemblies at Surfaces: Nanopatterning, Functionality, Reactivity" symposium to be held during the 2015 PACIFICHEM conference. The requested support will cover a portion of the meeting registration costs for invited speakers and symposium organizers.
Molecular assembly at surfaces is a burgeoning field dealing with the use of hydrogen bonds, metal-organic coordination and van der Waals forces to form two-dimensional long range ordered patterns. The proposed symposium will span 2 days and will feature seminars from world renowned speakers who will discuss cutting edge

15. SUBJECT TERMS
self-assembly, surface polymerization, scanning probe microscopy

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Dmitrii Perepichka
UU	UU	UU	UU		19b. TELEPHONE NUMBER 151-439-8623

Report Title

Final Report: Symposium "Supramolecular Assemblies on Surface: Nanopatterning, Functionality and Reactivity"

ABSTRACT

Funds are requested to provide support for the "Supramolecular Assemblies at Surfaces: Nanopatterning, Functionality, Reactivity" symposium to be held during the 2015 PACIFICHEM conference. The requested support will cover a portion of the meeting registration costs for invited speakers and symposium organizers.
Molecular assembly at surfaces is a burgeoning field dealing with the use of hydrogen bonds, metal-organic coordination and van der Waals forces to form two-dimensional long range ordered patterns. The proposed symposium will span 3 days and will feature seminars from world-renowed speakers who will discuss cutting-edge research related to functional supramolecular structures at surfaces as well as surfaced-confined reactions, including the bottom-up synthesis of linear conjugated polymers and two-dimensional polymers.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

69

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received	Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Post Doctorates

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Faculty Supported

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Technology Transfer

Technical Report on the US Army Grant

Symposium "Supramolecular Assemblies on Surface: Nanopatterning, Functionality and Reactivity"

68367CHCF, Agreement #W911NF-16-1-0036

Responsible: Dmitrii F. Perepichka (McGill University, Canada)

The funds were used to support invited speakers in the symposium #346 “Supramolecular Assemblies on Surface: Nanopatterning, Functionality and Reactivity" held on 18-20 December 2016 in Honolulu, HI, as a part of PACIFICHEM-2015 international conference. It was organized and co-chaired by Prof. Dmitrii Perepichka (McGill University, Canada), Prof. Federico Rosei (INRS, Canada), Prof. Paul Weiss (UCLA, USA), Prof. Andrew Wee (National University of Singapore) and Prof. Chen Wang (National Centre for Nanoscience and Technology, China).

The symposium included 6 oral sessions (3 morning, 2 afternoon and 1 night session) and 1 poster session. It featured 24 invited talks from leading scientist in the field, 23 contributed oral talks and 21 poster presentation, selected among submitted abstracts based on their quality & topic fit for the symposium. The presentations and associated discussion have explored three main themes: understanding and control of molecular self-assembly on surfaces; use of surface as template to grow novel 2D materials from molecular building blocks; use the surface-applicable nanotools (primarily, scanning probe microscopy and related spectroscopic methods) to study the functionality of molecular and polymeric materials at the nanoscale.

This was a 3rd symposium on the topic (1st was held as a Zing conference in Lanzarotte, Spain in 2012; the 2nd was held during ACS Spring meeting in Dallas in 2014). This series has clearly helped shaping the field which capitalizes on the use of nanoscience tools to investigate molecular behavior on surfaces and apply this knowledge to create novel nanomaterials. The current achievements and perspectives of the field, as it was communicated during the symposium, will be summarized as a Review Article co-authored by five co-organizers (invited review for *ACS Nano*, in preparation)

The table below lists the authors and titles of all papers presented during the symposium. The abstract of all invited talks is also attached at the end.

#346 Supramolecular Assemblies on Surfaces: Nanopatterning, Functionality, Reactivity

Fri, Dec 18 am - Sun, Dec 20 am

Presenting Author	Title	Presenter Institution	Start	End Time	Day	Dura
De Feyter, Steven	Molecular self-assembly on graphene and graphite: from fundamentals to applic	*KU Leuven*	8:05 AM	8:35 AM	Frida	**30**
Wang, Dong	Surface chirality: origin, propagation, and amplification	*Institute of Chemistry, CAS*	8:35 AM	9:05 AM	Frida	**30**
Schmidt, Nico	On surface tailoring of one- and two-dimensional supramolecular structures via l	*University of Groningen*	9:05 AM	9:25 AM	Frida	**20**
Bazuin, C. Geraldine	Diverse 2D patterns in supramolecular block copolymer thin films by dip-coating	*Université de Montréal*	9:25 AM	9:45 AM	Frida	**20**
	break					
Ritcey, Anna	Organized metal nanoparticle assemblies by block copolymer templating	*Université Laval*	10:00 AM	10:20 AM	Frida	**20**
Tahara, Kazukuni	Multi-component 2D self-assemblies at the liquid/solid interface via optimizatior	*Osaka University*	10:20 AM	10:40 AM	Frida	**20**
Mali, Kunal	Competing sergeant-soldiers and host-guest chirality induction pathways at the l	*KU Leuven*	10:40 AM	11:00 AM	Frida	**20**
Tait, Steven	Redox non-innocent ligand design for two and three electron oxidations of single	*Indiana University*	11:00 AM	11:30 AM	Frida	**30**
Beton, Peter	Supramolecular organisation on layered semiconductors and insulators	*University of Nottingham*	11:30 AM	12:00 PM	Frida	**30**
Tobe, Yoshito	On-surface host-guest chemistry of planar pyridine macrocycles with organic cat	*Osaka University*	1:00 PM	1:30 PM	Frida	**30**
Kim, Yousoo	Supramolecular assembly through ion-dipole interaction	*RIKEN*	1:30 PM	2:00 PM	Frida	**30**
Hipps, K W	Desorption rates and energy of desorption measurements at the solid solution ir	*Washington State U*	2:00 PM	2:30 PM	Frida	**30**
Anggara, Kevin	Clocking surface-reaction by the nosberved in-plane rotation of product	*University of Toronto*	2:30 PM	2:50 PM	Frida	**20**
Brothers, Penelope	Molecular Quasicrystals: Penrose Tiling With Molecules	*U of Auckland; MacDiarmid Ir*	2:50 PM	3:10 PM	Frida	**20**
	break					
Fu, Chaoying	Hydrogen-bonding in Control of Supramolecular Ordering of Organic Semicondu	*McGill University*	3:20 PM	3:40 PM	Frida	**20**
Lingenfelder, Magali	Tuning the Self-assembly of 5-amino [6]helicene on Solid Surfaces	*MaxPlanck-EPFL Lab for Mol.*	3:40 PM	4:00 PM	Frida	**20**
Hecht, Stefan	Towards spatio-temporally resolved chemistry: The role of surface confinement	*Humboldt-Universität zu Berl*	4:00 PM	4:30 PM	Frida	**30**
Bao, Zhenan	Self-assembly of organics on carbon surfaces and applications for electronic devi	*Stanford University*	4:30 PM	5:00 PM	Frida	**30**
~~Chi, Lifeng~~	~~Selective C-H Activation and C-C Coupling on Metal Surfaces~~	~~*Soochow U.; U of Muenster*~~	~~8:00 AM~~	~~8:30 AM~~	~~Satur~~	~~**30**~~
Lackinger, Markus	On-surface polymerization – a versatile synthetic route to novel 2D organic mate	*Deutsches Museum; TUM*	8:30 AM	9:00 AM	Satur	**30**
Tran, Bay	Bromine-functionalized pyrene derivatives on Au(111): self-assembly and on-sur	*University of Groningen*	9:00 AM	9:20 AM	Satur	**20**
Han, Patrick	Molecular-assembly mechanism enables simultaneous fabrication and connectio	*Tohoku Univ; UCLA*	9:20 AM	9:40 AM	Satur	**20**
	break					
Enache, Mihaela	A comparative study of two perylene derivatives on Cu(111): Insight into the bor	*University of Groningen*	9:55 AM	10:15 AM	Satur	**20**
Greenwood, John	Covalent modification of graphene and graphite using diazonium chemistry: Tun	*KU Leuven*	10:15 AM	10:35 AM	Satur	**20**
Hirose, Takashi	Photoresponsive supramolecular assemblies composed of photochomic diarylet	*Kyoto University*	10:35 AM	10:55 AM	Satur	**20**
KUNITAKE, Masashi	Thermodynamic Self-Assembly of 2-D/3-D Nanoarchitectures Constructed on Sol	*Kumamoto University*	10:55 AM	11:25 AM	Satur	**30**
Zimmt, Matthew	Patterning and Cross-linking of Self-Assembled Monolayers	*Brown University*	11:25 AM	11:55 AM	Satur	**30**

#346 Supramolecular Assemblies on Surfaces: Nanopatterning, Functionality, Reactivity

Fri, Dec 18 am - Sun, Dec 20 am

Presenting Author	Title	Presenter Institution	Start	End Time	Day	Dura
Grill, Leonhard	Testing functional molecular assemblies by single-molecule manipulation	*University of Graz*	1:00 PM	1:30 PM	Satur	30
Lin, Nian	Create and manipulate quantum states on surface using molecules	*HKUST*	1:30 PM	2:00 PM	Satur	30
Hla, Saw	Synchronization in Self-Assembled Molecular Machine Networks	*Ohio U.; Argonne Nat. Lab.*	2:00 PM	2:30 PM	Satur	30
Kawai, Maki	Spin state of Iron phthalocyanine (FePC) on metal surfaces	*The University of Tokyo*	2:30 PM	2:50 PM	Satur	20
Batteas, James	Modulating Charge Transport Mechanisms by Tuning the Architectures of Suprar	*Texas A&M University*	2:50 PM	3:10 PM	Satur	20
	break					
Ivasenko, Oleksandr	Electric-field-induced phase transformations at nanoscale	*KU Leuve*	3:20 PM	3:40 PM	Satur	20
Ye, Tao	Single molecule chemistry for surface assembly of DNA nanostructures	*Univ. of California, Merced*	3:40 PM	4:00 PM	Satur	20
Bartels, Ludwig	Anthraquinone and pentaquinone pores on Cu(111): network formation through	*Univ. of California, Riverside*	4:00 PM	4:30 PM	Satur	30
Barth, Johannes	Design and manipulation of functional molecular nanosystems at interfaces	*TUM*	4:30 PM	5:00 PM	Satur	30
Attias, Andre-Jean	Surface-confined self-assembled Janus tectons: a versatile platform for the nonc	*Pierre et Marie Curie Univ.*	7:00 PM	7:30 PM	Satur	30
Uemura, Shinobu	Self-assembly of heptazine derivatives at solution–electrode interfaces under ele	*Kagawa University*	7:30 PM	7:50 PM	Satur	20
Cometto, Fernando	Local Conformational Switching of Supramolecular Networks at the Solid/Liquid I	*MaxPlanck-EPFL Lab for Mol.*	7:50 PM	8:10 PM	Satur	20
~~Yuan, Jinying~~	~~Surface modified with Supramolecular Assemblies and its Electrochemical Respo~~	~~*Tsinghua University*~~	~~8:10 PM~~	~~8:30 PM~~	~~Satur~~	~~20~~
Costantini, Giovanni	Je t'aime … moi non plus, or how molecular self-assembly reveals the electronic	*University of Warwick*	8:30 PM	9:00 PM	Satur	30
Borguet, Eric	Supramolecular gateways to single molecule electronic properties	*Temple University*	8:00 AM	8:30 AM	Sund	30
Stoehr, Meike	Supramolecular assemblies on surfaces from cyano-functionalized molecules	*University of Groningen*	8:30 AM	9:00 AM	Sund	30
Otero, Roberto	Stoichiometry and Electronic Structure of Bidimensional Donor/Acceptor Superla	*U. Autónoma de Madri*	9:00 AM	9:30 AM	Sund	30
Adisoejoso, Jinne	Doping of graphene through physisorbed self-assembled monolayers	*KU Leuven*	9:30 AM	9:50 AM	Sund	20
Horton, Hugh	N-heterocyclic carbenes on gold: forming an ultra-stable self-assembled monola	*Queen's University*	9:50 AM	10:10 AM	Sund	20
	break					
Sakaguchi, Hiroshi	Graphene Nanoribbons Produced by 2-Zoned Chemical Vapor Deposition	*Kyoto University*	10:20 AM	10:50 AM	Sund	30
Loh, Kian	Template-assisted Self-Assembly of MoSx molecular wires and nanoribbons	*National Univ. of Singapore*	10:50 AM	11:20 AM	Sund	30
Bhattarai, Ashish	Processes at the solution-solid interface: Desorption rates and activation energy	*Washington State Univ*	11:20 AM	11:40 AM	Sund	20
Lehr, Joshua	Anion sensing supramolecular monolayers	*University of Oxford*	11:40 AM	12:00 PM	Sund	20

#346 Supramolecular Assemblies on Surfaces: Nanopatterning, Functionality, Reactivity

Fri, Dec 18 am - Sun, Dec 20 am

Poster Session, Fri, Dec 18th, 19:00-21:00

Zhao, Jianli	3D printing of functional nanostructures	*University of California, Davis*	**0**
Yu, Yan-Yan	Unique adsorption behaviors of carboxylic acids at rutile TiO2(110)	*East China University of Science and Technology*	**0**
Phan, Thanh Hai	Dual component grafting of HOPG: Towards large scale morphology control	*Division of Molecular Imaging and Photonics; Physics D*	**0**
Peng, Hui	Architectural control of surface properties and morphology of fluoromethacrylat	*The University of Queensland*	**0**
YAO, Shigeru	Supramolecular interaction of side chain crystalline polymer and interaction func	*Fukuoka University*	**0**
Shaw, Wendy	The structure and disassembly of a biomineralization protein on a biologically rel	*Pacific Northwest National Lab*	**0**
Higashi, Nobuyuki	Superhydrophobic surfaces via hierarchical layer-by-layer deposition on a lotus l	*Doshisha University*	**0**
Konishi, Tsubasa	Development of surface control technique by the photoresponsive self-assemble	*Kanagawa University*	**0**
Sato, Katsunori	Construction of calix crown-containing polymer nanosheets for capturing cesium	*Waseda Univ.*	**0**
Honda, Akinori	Self-assembled structures of alkyl-derivatized diketopyrrolopyrrole pigment at su	*Tokyo University of Science*	**0**
Han, Gyeongyeop	Chemical functionalization of two-dimensional surfaces with non-biofouling poly	*Kyungpook National University*	**0**
NISHITANI, Nobuhiko	STM Observation of Nucleation–Elongation Process of Surface-Confined Self-Ass	*Graduate School of Engineering, Kyoto University, Kyoto*	**0**
Okada, Kohei	Competitive adsorption of water and surfactants at solid/ionic liquid interfaces	*Tokyo University of Science*	**0**
Yin, Xueqiong	Preparation and hemocampatibility of electrospun nanofibers from bacterial cell	*Hainan University*	**0**
Lin, Weifeng	Scanning Tunneling Microscopy Investigation on Nanoparticle Packing Driven by	*University of California, Davis*	**0**
Urino, Hiroto	Orientation and Photofunctional Properties of the Thin Films of Oligothiophene I	*Toho University*	**0**
Yang, Jeonghyeon	Arrangement and reorganization of gold nanoparticles on nanolines prepared by	*Gyeongsang national university*	**0**
Iritani, Kohei	Construction of two-dimensional cyclic array of zinc porphyrin derivative and bin	*Osaka University*	**0**
Morita, Kotaro	Self-assembled structures of alkoxy-derivatized Ni(II)-salen complex investigated	*Tokyo University of Science*	**0**
Bhattarai, Ashish	Desorption kinetics at the solution-graphite interface: An STM study	*Washington State University-Pullman*	**0**
Ueji, Kan	Thermally activated transition with accompanying dimensional variation: Squaric	*Tokyo University of Science; RIKEN*	**0**

1833 - Molecular self-assembly on graphene and graphite: From fundamentals to applications

***Steven De Feyter**, steven.defeyter@chem.kuleuven.be*
Chemistry, KU Leuven, Leuven, Belgium, Belgium

Abstract Body: Nanostructured monolayers of molecules can be formed at a variety of interfaces. At a liquid-solid interface, such two-dimensional (2D) molecular assemblies can be created by depositing a solution of the compound of interest on top of the substrate (drop casting) or by immersing the substrate into a solution (dip coating). Very often, only weak non-covalent interactions govern the interplay between molecules and molecules and substrate. Advanced interface specific methods such as scanning tunneling microscopy (STM) and atomic force microscopy (AFM) provide structural and other types of information at the nanoscopic level.

In this presentation, we focus on several aspects of molecular self-assembly at the interface between a liquid or air, and substrates such as highly oriented pyrolytic graphite and graphene. Highly oriented pyrolytic graphite can be considered as an excellent model surface for adsorption and self-assembly of molecules on graphene. We will reveal novel concepts of 2D crystal engineering including the effect of solvent, solute concentration and temperature, stimulus-driven self-assembly and self-assembly under nanoconfinement conditions, bringing insight into thermodynamic and kinetics aspects of the self-assembly process at the interface between a liquid and graphite or graphene.

Based on these insights, we will demonstrate molecular self-assembly based functionalization of graphite and graphene. Various applications will be presented, including tunable doping of graphene based field effect transistors.

1834 - Surface chirality: Origin, propagation, and amplification

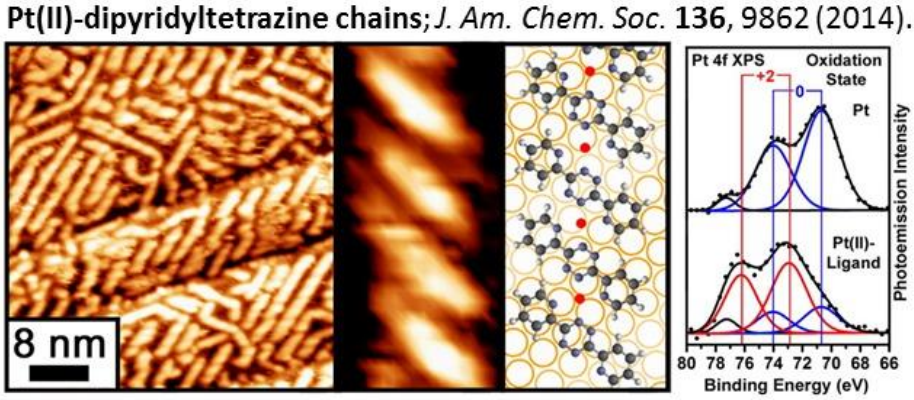
***Dong Wang**, wangd@iccas.ac.cn, Ting Chen, li-Jun Wan*
Institute of Chemistry, CAS, Beijing, China

Abstract Body: Two-dimensional (2D) chirality in molecular self-assembly on solid surfaces has gained wide interests because of its fundamental significance and application potentials. Through the adsorption of chiral molecules, 2D chirality can be endowed to achiral solid surfaces. Besides, self-assembly of achiral molecules on achiral surfaces could induce 2D chirality due to reduced freedom and the constraint of substrate lattice. However, the spontaneous resolution of achiral molecules into 2D enantiomorphous assemblies shows no chiral bias and typically leads to globally racemic surfaces. We herein report the induction of global homochirality in 2D enantiomorphous networks of achiral molecules via co-assembly with chiral co-adsorber. We further show that the global homochirality of the network assembly depends nonlinearly on the enantiomeric excess of chiral co-adsorber in the solution phase, demonstrating the validation of the "majority-rules" for the homochirality control of achiral molecules at liquid/solid interface. Such an induction and nonlinear chirality amplification effect promises new approach towards 2D homochirality control and sheds important insights into asymmetric heterogeneous catalysis, chiral separation, and chiral crystallization.
References:
(1) Chen, T.; Yang, W. H.; Wang, D.**;** Wan, L.-J. *Nature Commun*. **2013**, *4*, 1389
(2) Chen, T.; Li, S.-Y.; Wang, D.; Yao M.; Wan, L.-J. *Angew. Chem. Int. Ed*. **2015**, *54*, 4309

1840 - Redox non-innocent ligand design for two and three electron oxidations of single-site metal centers at surfaces

***Steven Tait**, tait@indiana.edu*
Chemistry, Indiana University, Bloomington, Indiana, United States

Abstract Body: Systematic tuning of metal centers on surfaces could provide new methods for increased selectivity in heterogenous catalysis. Supramolecular self-assembly and redox chemistry at surfaces provide a promising route to engage the broad capabilities in organic ligand design, commonly used in homogeneous catalysis, to address selectivity challenges in surface catalysts. The formation of chemically and structurally uniform single-site centers at surfaces by on-surface redox chemistry from metallic precursors has recently been demonstrated by our group with platinum, chromium, iron, and vanadium vapor deposited with organic ligands on a Au(100) surface (*J. Am. Chem. Soc.* 2014, **136**, 9862-9865; *J. Chem. Phys.* 2015, **142**, 101913; and newly submitted work). To probe the extent of oxidation state control in these systems, tetrazine-based ligands were designed and co-deposited with vanadium metal, which is an excellent candidate for probing access to a variety of oxidation states. The oxidizing power of the tetrazine species is tuned by peripheral functional groups to access two and three electron oxidation processes, as determined by X-ray photoelectron spectroscopy (XPS). Platinum(II) centers have also been formed with these ligands. In each of these cases, the metal-ligand complexes take the form of nearly identical one-dimensional polymeric chains, resolved by molecular-resolution scanning tunneling microscopy (STM). These structures provide highly uniform quasi-square-planar coordination sites for the metal, which contributes to the well-defined chemical state of the metal. This strategy is also applied to earth-abundant metals such as iron and chromium using commonly available phenanthroline ligands and is allowing us to develop understanding of how to control and program single-site metal centers on surfaces for next-generation catalysis.



Pt(II)-dipyridyltetrazine chains formed by redox reaction on the Au(100) surface. STM images show chain structure and XP spectroscopy reveals change in oxidation state of the metal. See *J. Am. Chem. Soc.* **136**, 9862 (2014).

1841 - Supramolecular organisation on layered semiconductors and insulators

Vladimir Korolkov[1], Alex Summerfield[1], James Kerfoot[1], Simon Svatek[1], Nick Besley[1], Neil Champness[1], Lixu Yang[1], Kenji Watanabe[2], Takashi Taniguchi[2], ***Peter Beton****[1], peter.beton@nottingham.ac.uk*
[1] University of Nottingham, Nottingham, United Kingdom; [2] NIMS, Tsukuba, Japan

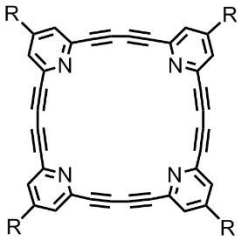
Abstract Body: The depsoition and supramolecular ordering of organic molecules on the layered materials hexagonal boron nitride (hBN) and molybdenum disulphide has been investigated using atomic force microscopy under ambient conditions. We show that it is possible to deposit highly ordered arrangements of molecules with sub-monolayer to few monolayer coverage, either from solution or by sublmation, on these surfaces and acquire images with sub-nanometre resolution facilitating the identification of modes of molecular organisation. We find that the deposition of tetrakis (4-carboxyphenyl) prophyrin leads to the formation of an open regular square arrangement stabilised by hydrogen bonding which co-exists with a honeycomb array with dimensions which are in good agreement with calculated values. It is also possible to form, and image with molecular resolution, monolayers of perylene tetracarboxylic di-imide, both as a single species and in combination with melamine when it forms a honeycomb network similar to that observed previsouly on other surfaces. The resolution which may be attained using ambient AFM shows some intramolecular contrast for these materials. We have also investigated the adsorption of C_{60} using both sublimation and solution depsition. From solution we see exclusively bilayers but sublimed films show a complex temperature-dependenet morphology with multiulayer dendritic islands formed at room temperature, but at higher temperature bilayers and monolayers are formed and we relate these observations to recent reports of de-wetting of C_{60} on alkali halide surfaces. The hBN flakes, which are prepared by exfoliation from mm-scale single crystals, have a large band-gap facilitating optical investigations and we discuss progress towards the acquisition fo fluorescence measurements on these systems.

1993 - On-surface host-guest chemistry of planar pyridine macrocycles with organic cations

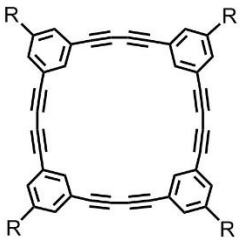
***Yoshito Tobe**, tobe@chem.es.osaka-u.ac.jp*
Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka, Japan

Abstract Body: Whereas there are numerous examples of host-guest binding between mocrocylcles bearing interior donor groups and positively charged species via ion-dipole interactions, little has been known for the correspnding events on surfacces despite their relevance to potential applications. Previously, we reported that square pyridine macrocyle **1a** and the corresponding benzene macrocycle **2c** self-assembled at the interface of organic solvent and graphite, forming a square tiling pattern of one-dimensional order in which tropylium ion **3** was bound selectively to **1a**.[1] Recently we disclosed the formation of square tiling of two-dimensional order consisting of **1a**,**b** and **2b**-**d**, wherein **3** was bound selectively to **1a**,**b**.[2] Moreover, hexagonal pyridine macrocycle **4** was found to form a hexagonal packing pattern. Interestingly, binding with triazatriagulenium ion **5** induced the packing structure change most likely due to a biased binding location of **5** in the pore of **4**.

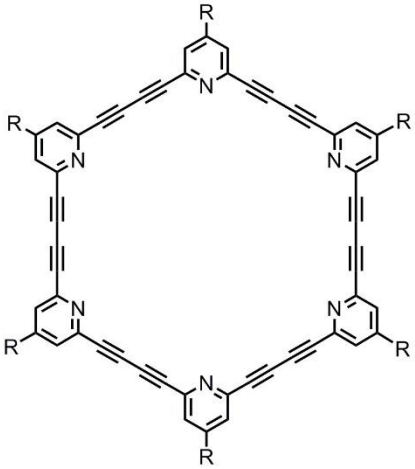
[1] Tahara, K.; Lei, S.; Mamdouh, W.; Yamaguchi, Y.; Ichikawa, T.; Uji-i, H.; Sonoda, M.; Hirose, K.; De Schryver, F. C.; De Feyter, S.; Tobe, Y. *J. Am. Chem. Soc.* **2008**, *130*, 6666–6667.
[2] Tahara, K.; Gotoda, J.; Carroll, C. N.; Hirose, K.; De Feyter, S.; Tobe, Y. *Chem*. *Eur*. *J*. in press. DOI: 10.1002/chem.201500026.



1a R=$CO_2C_8H_{17}$
1b R=$CH_2OC_8H_{17}$

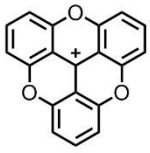


2a R=$CO_2C_8H_{17}$
2b R=$CH_2OC_8H_{17}$
2c R=OC_9H_{19}
2d R=$C_2H_4OC_7H_{15}$



4 R=$CH_2OC_8H_{17}$

3



5

1994 - Supramolecular assembly through ion-dipole interaction

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Abstract Body: Establishing a way to fabricate well-ordered molecular structures is a necessary step towards advancement in molecule-based devices. Especially, fabrication of homogeneous organic monolayer requires precise control of intermolecular interactions and molecule-substrate interactions. There have been reported tremendous number of attempts to form well-ordered organic monolayers by employing various kinds of intermolecular interactions such as covalent bonds, hydrogen bonds, electrostatic interactions, and van der Waals interaction, according to the degree of strength. Here, I will introduce some of our experimental results of tuning intermolecular interactions to control organic monolayer formation [1-4]. My talk will mainly focus on fabrication of a well-developed homogeneous monolayer of diarylethene molecules on the Cu(111) surface with the aid of NaCl co-deposition [5], on the basis of interactions between molecular dipoles and alkali metal ions, which is weaker than covalent bonding but is stronger than dipole-dipole interaction and van der Waals interaction.

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2. T. K. Shimizu, J. Jung, T. Otani, Y.-K. Han, M. Kawai, and Y. Kim, ACS Nano 6 (2012) 2679-2685.
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4. K. Ueji., J. Jung., J. Oh, K. Miyamura, and Y. Kim, Chem. Commun. 50 (2014) 11230-11233.
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1995 - Desorption rates and energy of desorption measurements at the solid solution interface

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Abstract Body: Scanning tunneling microscopy (STM) was used to measure molecular scale temperature dependent desorption rates and desorption energies for cobalt(II) octaethylporphyrin (CoOEP) and nickel(II) octaethylporphyrin (NiOEP) at the phenyloctane solution-HOPG interface. At lower temperatures, monolayer formation of MOEP on HOPG from solution was found to be completely controlled by kinetics and the adlayer formed was stable up to 70 ^{0}C. Measurable molecular desorption of CoOEP from the HOPG surface was observed above 80 ^{0}C. CoOEP desorbs from HOPG into phenyloctane at a rate of 0.0056 ± 0.0003 min^{-1} at 90 ^{0}C, 0.014 ± 0.001 min^{-1} at 100 ^{0}C, and 0.034 ± 0.002 min^{-1} at 110 ^{0}C. The activation energy of molecular desorption at the solution-solid interface was determined assuming an Arrhenius dependence. The desorption energy of CoOEP from HOPG into phenyloctane was determined to be 1.04 x 10^2 ± 0.029 x 10^2 kJ/mol. NiOEP desorption occurs at a slower rate and is homogeneous across HOPG terraces, unlike the inhomogeneous desorption observed on Au(111). The calculated desorption rate of CoOEP from HOPG at 135 ^{0}C in this work is 0.22 min^{-1}, making it 1000 times greater than from Au(111). The monolayer formation process is very fast. For solution concentrations of the order of 120 μM, a dense monolayer is formed within seconds. The surface coverage on both HOPG and Au(111) surfaces was determined by the relative concentration of each species in solution. The rates of adsorption of NiOEP and CoOEP (for concentrations near 100 μM) are found to be within 20% of each other. The difference in the desorption rates on HOPG and Au(111) arises from differences in adsorbate-substrate interactions.

2000 - Toward spatio-temporally resolved chemistry: The role of surface confinement

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Abstract Body: The foundation of the chemical enterprise has always been the creation of new molecular entities, such as pharmaceuticals or polymeric materials. Over the past decades, this continuing effort of designing compounds with improved properties has been complemented with a strong effort to render their preparation (more) sustainable by implementing atom as well as energy economic strategies. However, besides being concerned with *what* and *how* to make, it should become increasingly important for chemists to control *when* and *where* chemical reactions take place.[1] The ultimate goal is to perform chemistry with high spatial and temporal resolution, which would allow to time reactions, for example in simple cascades or complex chemical networks, and to localize them, for example in 2D patterns for array chip technologies or even in 3D.
We seek to gain control over time and space of a chemical transformation of choice by two approaches: One using a gate, which upon the action of an external stimulus acts as a "remote control", and another exploiting surface-confined and tip-controlled reactivity. This presentation will focus on our activities in the latter field, where we have developed an on-surface polymerization route[2] to generate new hybrid materials, and discuss our most recent progress and highlight future challenges.

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2001 - Self-assembly of organics on carbon surfaces and applications for electronic devices

***Zhenan Bao**, zbao@stanford.edu*
Chemical Engineering, Stanford University, Stanford, California, United States

Abstract Body: In this talk, I will discuss two examples of the applications of self-assembly chemistry on carbon surfaces, namely on carbon nanotube and graphene surfaces, for electronics applications. In one example, we investigated the self-assembly of conjugated polymers and supramolecular polymers on carbon nanotubes for the sorting of semiconducting carbon nanotubes. In another example, I will describe the self-assembly of organic semiconductors on graphene surface for high performance vertical transistors.

2268 - On-surface polymerization – a versatile synthetic route to novel 2D organic materials

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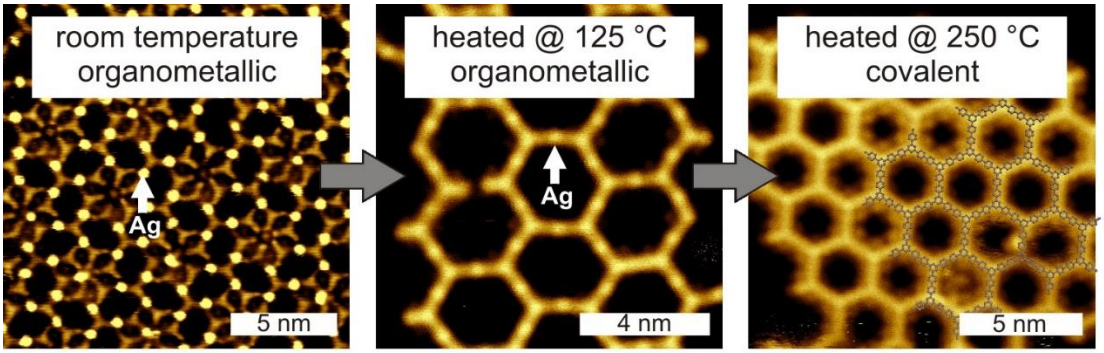
Abstract Body: Flat surfaces appear to be the ideal template for the synthesis of regular covalently cross-linked organic 2D materials. Surfaces can not only topologically confine the reaction into two dimensions, but can also play an active chemical role for the polymerization. Hence, the material and crystallographic orientation of the surface can also be used to steer or even control the reaction. The main objective of the lecture is to critically discuss the status, the main challenges, and the potential of on-surface polymerization for the synthesis of novel organic 2D materials.

Different coupling reactions were already employed in a surface-chemical approach, each with specific advantages and disadvantages. An important distinction is whether the reaction can be carried out under slightly reversibly conditions or necessarily remains fully irreversible. While polymerization close to thermodynamic equilibrium opens up ways to improved structural quality, purely kinetically controlled reactions apparently inevitably lead to highly defective networks. An instructive example for the first is the synthesis of 2D Covalent Organic Frameworks by boronic acid condensation. On the other side, on-surface Ullmann coupling is a kinetically controlled reaction which is widely employed for the synthesis of 1D and 2D organic nanostructures. Using Ullmann coupling as an example a detailed view will be presented on the surface-dependence, possible reaction intermediates, and the relation between defects and kinetic reaction parameters. Finally, the potential of metastable intermediate organometallic networks to improve the structural quality of 2D polymers will be demonstrated.

[1] ACS Nano 8, 7880 – 7889 (2014).
[2] Chem. Commun. 50, 7680 – 7682 (2014).
[3] ACS Nano 7, 3014 – 3021 (2013).



2274 - Thermodynamic self-assembly of 2D/3D nanoarchitectures constructed on solid/liquid interfaces

***Masashi Kunitake**, kunitake@kumamoto-u.ac.jp*
Graduate School of Science and Technology, Kumamoto University, Kumamoto, Japan

Abstract Body: The construction of sophisticated, supramolecular architectures through self-assembly has attracted considerable attention as “bottom-up” nanotechnology. A general substrate-mediated, soft solution methodology for the preparation of polymeric nanoarchitectures will be discussed from the aspect of thermodynamic self-assembly. The Schiff base coupling reaction would be one of suitable covalent coupling reaction to construct 2-D macromolecular frameworks, because it is a dynamic reversible reaction that can be thermodynamically managed by fine tuning of the reaction conditions based on ‘adsorption (partition)-desorption’ and ‘coupling-decoupling’ equilibria. Then, 2-D covalent nanoarchitectures produced by spontaneous and selective linkage of building block molecules, and were formed on hydrophobic substrates from aqueous solutions in the presence of simple building block molecules under ambient conditions. Furthermore, colorful π-conjugated nanofilms with unique mesostructures were found to be also formed via consecutive chemical liquid deposition from a similar aqueous solution with a slightly different reaction condition. This low-cost and eco-friendly ‘bottom-up’ methodology paves the way to a ‘bottom-up’ assembly of a vast array of solid-supported, designer supramolecular nanoarchitectures with potential use as functional materials for applications including but not limited to next-generation organic electronics.

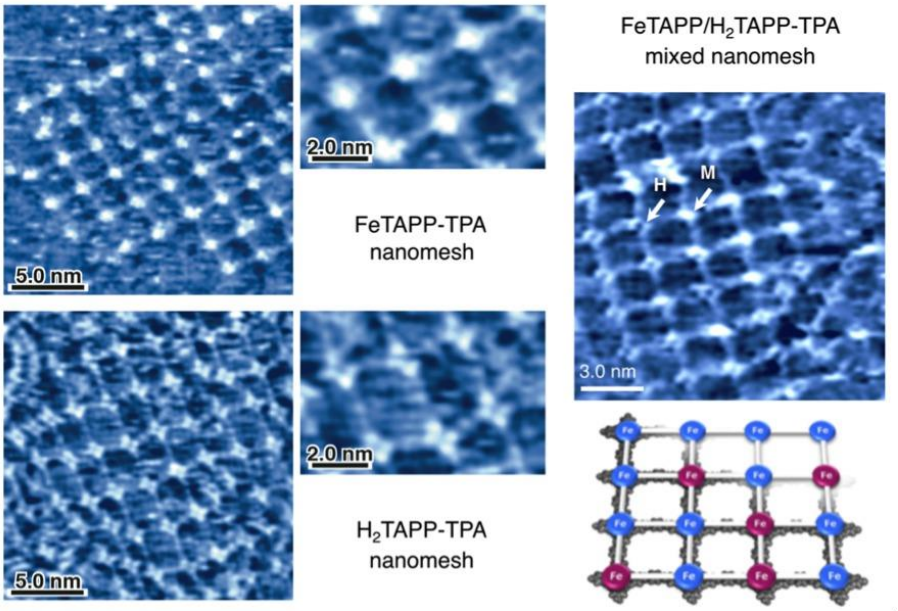


Figure 1 Discrimination of metal & metal-free porphyrin in covalent 2-D porphyrin mesh

2275 - Patterning and cross-linking of self-assembled monolayers

***Matthew Zimmt**, mbz@brown.edu, Yan Yang, Jian He, Chen Fang, Russell Shelp*
Chemistry, Brown University, Providence, Rhode Island, United States

Abstract Body: Monolayers with remarkably complex molecular patterns can be formed by supramolecular self-assembly at surfaces. Applications of patterned monolayers, e.g. as ultra-high resolution templates, require incorporation of reactive entities to lock-in pattern order and to interact with added template targets. The structures and chemical reactions of reactive entities should not disrupt pattern formation and should be facile at the surface. This presentation will report efforts to perform and characterize in-layer and off-layer cross-linking to lock-in patterned assembly structure and to advance template function.

2535 - Testing functional molecular assemblies by single-molecule manipulation

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Chemistry Department, University of Graz, Graz, Austria

Abstract Body: The use of functional molecules and their assembly into pre-defined architectures are key challenges in nanotechnology and of interest in various fields from molecular electronics over novel materials to molecular machines. A central challenge is in this regard to **maintain and potentially even extend the functionality of individual molecules upon integration into an assembly or a polymer**. We have incorporated functional molecules in supramolecular assemblies and covalent nanostructures and have tested them by single-molecule manipulation.
Several examples of functional molecules will be presented. Our focus is on the one hand on molecular switches that exist in at least two stable states that differ in their physical/chemical properties. Various such molecules will be presented, one of them are assemblies of porphycene molecules that not only maintain their switching behavior but even extend it to cooperative switching [1]. On the other hand, we have investigated different functional polymer structures and have characterized them in single-molecule pulling experiments [2] – various recent examples will be discussed.
[1] Nature Chem. 6, 41 (2014); [2] Proc. Nat. Acad. Sci. 111, 3968 (2014).

2536 - Create and manipulate quantum states on surface using molecules

***Nian Lin**, phnlin@ust.hk*
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Abstract Body: We demonstrate that molecular and supramolecular structures assembled on metal surface provide an effective means to control and manipulate two-dimensional electron gas (2DEG). The first example is to use a cryogenic scanning tunneling microscope to arrange coronene molecules one by one into a triangular lattice on a Cu(111) surface.[1] As revealed by tunneling spectroscopy, the band structure and density of states of the 2DEG exhibit hallmark signatures of massless Dirac fermions. We then manipulated the quasi-particle spectra with aperiodically-arranged molecules, including zigzag and arm-chair edge nanoribbons, single vacancies, Stone-Wales defects and grain boundary dislocation lines. We detected enhanced density of states at or close to the Dirac point. In particular, we resolved edge states in the zigzag nanoribbons. The second example is to use supramolecular self-assembly on a Cu(111) surface to modulate 2DEG band structures.[2] The characteristics of the bands are tuned though changing the periodicity of the supramolecular networks and the molecule-to-surface interaction. In the last, we present a proposal for engineering topological superconductors using this technique, which aims at probing Majorana fermions. [3]

[1] Phys. Rev. B. 88 (2013) 245430.
[2] Phys. Rev. Lett. 113 (2014) 196803.
[3] arXiv:1502.02548 (2015)

2537 - Synchronization in self-assembled molecular machine networks

Saw Hla[1,2]*, hla@ohio.edu*
[1] Physics & Astronomy, Ohio University, Athens, Ohio, United States; [2] Nanoscience and Technology Division, Argonne National Laboratory, Lemont, Illinois, United States

Abstract Body:A recent emergent research direction is the development of complex molecular machines suitable to operate on solid surfaces. Unlike biological counterparts, the synthetic molecular machines may tolerate a more diverse range of conditions, and thus be advantageous for the complex functions with low power consumption suitable to operate in solid state devices. Development of such molecular devices requires testing their operation mechanisms. We use low temperature scanning tunneling microscopy, spectroscopy, and molecular manipulation schemes to investigate fundamental operations of synthetic molecular switches and molecular motors on metallic surfaces [1-4]. In addition to single molecule operations, synchronization of molecular motors can be achieved depending on the symmetry of the molecular assemblies on surfaces and thus opening future development of solid state compatible complex molecular machines for potential applications.

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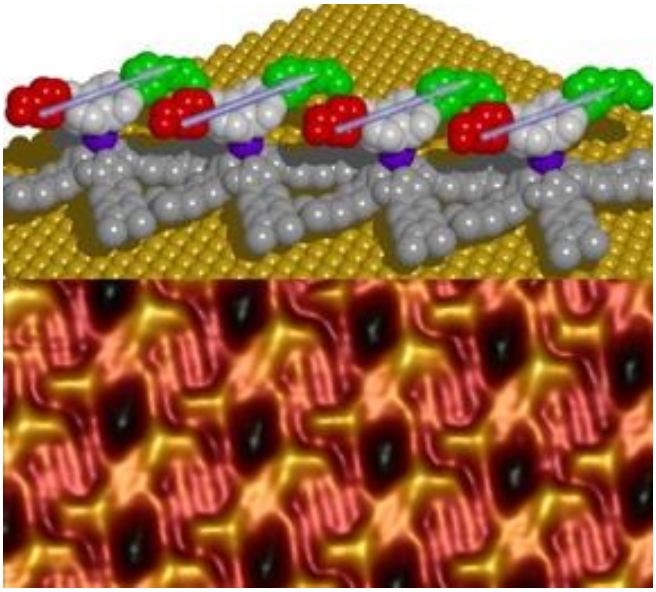
[2] V. Iancu, and S.-W. Hla, ***Proc. Nat. Acad. Sci.*** **103**, 13718-13721 (2006).
[3] Y.-S. Fu et al. ***Nano Lett.*** **12**, 3931-3935 (2012).
[4] U.G.E. Perera et al. ***Nature Nanotechnology*** **5**, 46-51 (2013).
[5] Y. Zhang et al., submitted.



2542 - Anthraquinone and pentaquinone pores on Cu(111): network formation through substrate electron confinement and its impact on guest dynamics

***Ludwig Bartels**, bartels@ucr.edu*
Chemistry, University of California, Riverside, California, United States

Abstract Body:Anthraquinone self-assembles on Cu(111) into an open honeycomb network with exactly three molecules on each side. Pentaquinone forms a very similar network with three molecules to each side, that results in a larger overall periodicity due to the pentaquinone's larger size. However, the exposed pore size is practically identical in both of these networks. The anthraquinone network in particular exhibits an astonishing degree of order despite the adsorption system's capability of forming larger, smaller and odd-shaped pores as well. Synchrotron-based mapping of the dispersion of the substrate surface state as a function of the anthraquinone coverage offers correlation of the total charge confined in the surface state in each pore with pore geometry and the spectrum of pore-confined states. The result reveals a remarkable coincidence between shell-filling, noble-gas-like electron arrangements within the pores and the preferred pore geometry. While the pore electronic states eluded direct imaging, their impact on the placement and dynamics of CO guest molecules inside the pores can be monitored directly. Titration of the pore electronic states by CO molecules reveals a tendency for arrangement according to the computational node structure of the electron distribution until the number of the pore-confined surface state electrons matches that of the CO guests.

2543 - Design and manipulation of functional molecular nanosystems at interfaces

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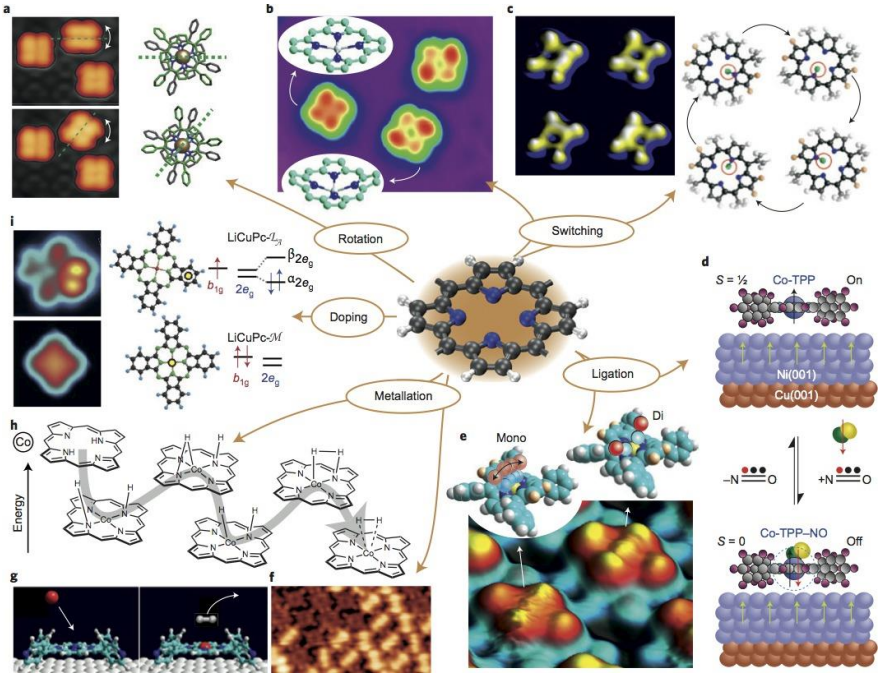
Abstract Body: The control and organization of molecular species at interfaces is key to advance molecular science, nanochemistry and the development of novel low-dim materials. The insights gained affect multiple fundamental and application fields, including catalysis, sensing, light-harvesting, molecular nanomagnetism & spintronics, organic electronics or single-molecule thermodynamics. We explore molecular modules, steer their organisational and dynamic behaviour, and afford novel functions using well-defined homogenous surfaces, textured and sp2-nanotemplates as construction platforms. The devised bottom-up fabrication protocols implement biological and *de novo* synthesized building blocks, while exploiting error-corrective noncovalent bonding and metal-directed assembly, as well as covalent chemistry. Scanning probe real-space observations visualize structural features with atomic precision, revealing molecular recognition, assembly and bonding schemes mediating the expression of distinct nanoarchitectures. Multitechnique studies of flexible species such as metalloporphyrins exemplify the delicate interplay between conformational adaptation, electronic signature or magnetic features with the bonding of adducts. Our approach provides a rationale for the interfacial control of single molecular units and the design of nanostructured materials with complex features, intricate dynamics and tunable functional properties. Complementary modeling efforts perfect the experimental insights, unravel underlying driving forces, and disentagle structure-functionality relationships or complex dynamic phenomena.



Functional properties and pathways to manipulate and control tetrapyrrole units confined at interfaces (10.1038/NCHEM.2159).

2711 - Surface-confined self-assembled Janus tectons: A versatile platform for the noncovalent functionalization of graphene

*PING DU[1], DAVID KREHER[1], FABRICE MATHEVET[1], FABRICE CHARRA[2], **ANDRE-JEAN ATTIAS**[1], andre-jean.attias@upmc.fr*
[1] Paris Institute of Molecular Chemistry - Polymer Chemistry Lab., Pierre et Marie Curie University, Paris, France; [2] CEA, Saclay, France

Abstract Body:A general strategy for simultaneously generating surface-based supramolecular architectures on flat sp^2-hybridized carbon supports and independently exposing on demand off-plane functionality with controlled lateral order is highly desirable in view of the noncovalent functionalization of graphene.
With this aim, we recently developed the Janus tecton concept, a new Janus material [1-2]. This is a molecular three-dimensional (3D) building blocks consisting of two faces linked by a cyclophane-type pillar. One face is designed to steer 2D self-assembly onto C(sp2)-carbon-based flat surfaces, the other allowing for the desired functionality above the substrate with a well-controlled lateral order.
Here, we provide for the first time a versatile molecular platform [1] based on a library of new 3D Janus tectons able to form surface-confined supramolecular adlayers [1-3] in which it is possible to simultaneously (i) steer the 2D self-assembly on flat sp^2-carbon based substrates [4] and (ii) tailor the external interface above the substrate by exposing a wide variety of small terminal chemical groups and functional moieties [1]. This approach is validated through the self-assembly study by scanning tunneling microscopy (STM) at the liquid-solid interface and molecular mechanics modeling. The successful self-assembly on graphene, together with the possibility to transfer the graphene monolayer onto various substrates, should considerably expend the domains of application of our functionalization strategy [1].

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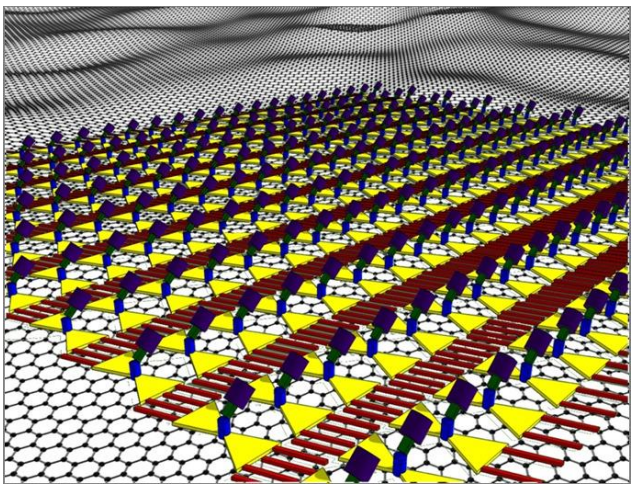
[2]. A. J. Attias et al. **Angew. Chem. Int. Ed.** 50, 6562, 2011.
[3]. A. J. Attias et al. **Angew. Chem. Int. Ed.** 47, 8412, 2008.
[4]. A. J. Attias et al. **Angew. Chem. Int. Ed.** 46, 7404, 2007.

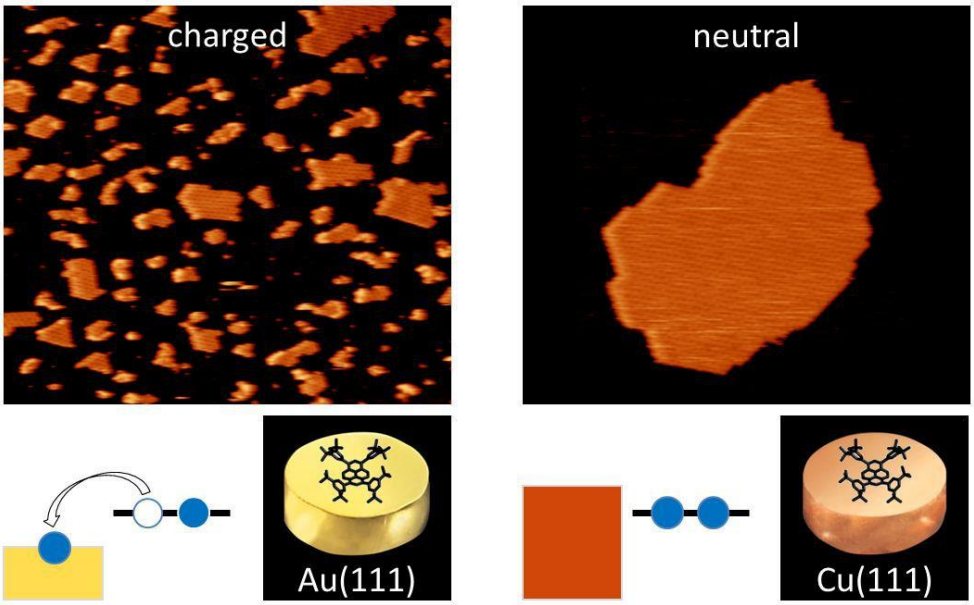


Scheme1: 2D self-assembly of Janus tectons on graphene

2715 - *Je t'aime … moi non plus*, or how molecular self-assembly reveals the electronic properties of metal-organic interfaces

***Giovanni Costantini**, g.costantini@warwick.ac.uk*
University of Warwick, Coventry, United Kingdom

Abstract Body: Most applications in organic electronics and organic photovoltaics require the deposition of a thin molecular film onto conductive electrodes. The growth of the first few molecular layers represents a crucial step in the device fabrication since the organic-electrode interface carries the entire device functionality. Nevertheless, the ability to rationally tune and modify the electronic configuration of these systems is extremely limited because the energy level alignment at metal-organic interfaces is influenced by a complex combination of factors. As a result, most work in the field is still based on a trial-and-error approach. In this talk I will present a new method to investigate the formation of metal-organic interfaces based on studying the relation between molecule-substrate charge transfer and the development of specific molecular assembly patterns. In particular, I will show that the driving force for charging an individual molecule depends not only on the position of its frontier orbitals with respect to the substrate Fermi level, but also on the electrostatic interaction with its local neighbours' environment. The resulting interplay of long-range attractive or repulsive forces acting between interfacial molecular dipoles and short-range attractive interactions, determines the emergence of peculiar assembly patterns that are a direct consequence of the local electronic configuration.
Using a series of ad-hoc designed molecules I will show that combining scanning tunnelling microscopy and spectroscopy with atomistic simulations allows to study the elementary processes responsible for the observed self-assembly behaviour. The talk will focus on molecules characterised by anomalous coarsening caused by reversible charge transfer [*ACS Nano* **2014**, *8*, 12356] and on two-component systems where specific co-assembly patterns result from the electron accepting behaviour of one molecule being selectively induced by the presence of the other [*in preparation*].



2832 - Supramolecular gateways to single molecule electronic properties

***Eric Borguet**, eborguet@temple.edu*
Chemistry, Temple University, Philadelphia, Pennsylvania, United States

Abstract Body: Molecular scale electronic devices usually are designed by wiring a single molecule between metal electrodes via anchoring groups. Conventional single molecule conductivity (SMC) studies focus on molecules with functional groups that provide efficient electronic coupling and bind the organic molecular backbone to the metal electrodes. However, conductance is sensitive to the atomic level details of the molecule-electrode contact so that the anchoring groups end up being resistive spacers between the molecule and the metal, decreasing the single molecule junction conductivity. Thus creating well-defined, highly conductive molecular junctions to minimize resistance introduced by chemical linkers is a challenging experimental problem especially under ambient conditions.

The conductivity of a single aromatic ring, perpendicular to its plane, is determined using a new strategy under ambient conditions and at room temperature using a combination of molecular assembly, Scanning Tunneling Microscopy (STM) imaging and STM break junction (STM-BJ) techniques. The construction of such molecular junctions exploits the formation of highly ordered structures of flat-oriented mesitylene on Au(111) to enable direct tip/π contacts, a result that is not possible via conventional methods. The measured conductance of sandwiched Au/π/Au junction is ~$0.1G_o$, two orders of magnitude higher than the conductance of phenyl rings connected via standard anchoring groups. A comparison with other benzene derivatives, that do not display long-range ordered structure, suggests that such structures, which hold the aromatic ring in place and parallel to the surface, are essential to the increased probability of the formation of orientation-controlled “sandwiched” molecular junctions. Extentions to molecular systems where different elements of the molecular conductance tensor can be measured and to switching between conductance pathways will be discussed.

2833 - Supramolecular assemblies on surfaces from cyano-functionalized molecules

***Meike Stoehr**, m.a.stohr@rug.nl*
Zernike Institute for Advanced Materials, University of Groningen, Groningen, Netherlands

Abstract Body: The interest in studying organic nanostructures on surfaces emerges from their prospective applications in nanoscale electronic or optoelectronic devices, in which the spatially addressable functional units are to be assembled on the molecular level. By making use of molecular recognition processes based on non-covalent interactions, well-ordered 1D and 2D molecular structures can be formed on surfaces. The understanding of the interplay of the underlying intermolecular and molecule substrate interactions is highly important since the resulting molecular structures are based upon these two interactions.
Cyano-functionalized molecules have gained increasing interest over the last years because the asymmetric charge distribution of cyano ligands leads to the formation of an intrinsic dipole, which can be involved in intermolecular dipolar coupling, hydrogen bonding or metal-ligand interactions. For the case of cyano-functionalized porphyrins, the adsorption on Au(111) and the effect of post deposition annealing will be discussed while for dicarbonitrile polyphenyl derivatives the adsorption behavior on Au(111) will be compared to the one on graphene.

2837 - Graphene nanoribbons produced by 2-zoned chemical vapor deposition

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Institute of Advanced Energy, Kyoto University, Uji, Kyoto, Japan

Abstract Body: Surface polymerization techniques are promising to fabricate novel materials on surface.[1,2] Graphene nanoribbon (GNR) which is predicted to behave as semiconductor, is a promising material for many applications. Compared with top-down method, bottom-up approaches have an advantage to produce GNRs with a defined edge-structure and widths. The bottom-up approaches reported to date include organic synthesis in solution, and surface-assisted growth in a ultra high vacuum (UHV) environment using the deposition of haloarenes on Au(111) substrate. Although these bottom-up methods provide GNRs with a defined edge structure, the methods reported to date suffer from the systematic synthesis of GNR having different width at larger scales because of the low solubility of GNRs and the need for special environments and instruments.
In this report, we demonstrated large-scale growth of all types of armchair-edged GNRs (3p, 3p+1, and 3p+2; p is defined as the number of carbon atoms along the width) on Au(111) even in extremely low-vacuum conditions using our newly developed method, 2-zoned radical-polymerized chemical vapor deposition (RP-CVD).[3] Armchair-edged GNRs with a width of 2, 3, or 4 benzene rings, grown on a large scale, can form the isolated films, which can be used to characterize the experimentally unknown width-dependent band gap and can also be used to fabricate devices such as field effect transistors (FETs) and photoconductive devices. Acene-typed GNRs could be also fabricated using this technique towards zigzag-edged GNRs.

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2838 - Template-assisted self-assembly of MoSx molecular wires and nanoribbons

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[1] Chemistry, National University of Singapore, Singapore, Singapore, Singapore; [2] Centre for Two Dimensional Materials and Graphene Research Centre, National University of Singapore, Singapore, Singapore

Abstract Body: Transition-metal disulfides (TMDCS) consisting of quasi-2D layers of MX_2(M, transition- metal atom; X, chalcogen atom) have attracted immense interests due to the presence of a band gap, high optical conductivity and large spin-orbit coupling. Other than 2-D, 1-D TMDCS quantum wires are interesting too due to its 1-D metallic conduction and charge density wave transition. Herein, we study the self-assembly of Mo and S atoms into ordered 1-D nanophases on the narrow step edges of Au vicinal (755) surface using atom-resolved scanning tunneling microscopy (STM). MoS_x (x<2) molecular wires were first pinned at the Au (100) step edges due to the selective adsorption of sulfur atoms and covalent bonding with Mo atoms beneath the first Au layer. Row by row replication of MoSx wires are replicated from the pre-formed wire along Au(100) step edges. Concentration-dependent surface stress drives the spontaneous transition of MoS_x wires into 1-D MoS_2 ribbon.
We have also studied the growth of an interesting MoSx phase showing square-like lattice on Cu (111), which attests to the rich structural diversity of molybdenum sulfide polytypes.